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Solar-Light-Assisted Photo-degradation of Azo Dyes Using Some Transition Metal Oxides

A.V. Salker

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1. Introduction

Heterogeneous photo-catalysis through illumination by solar light on a semiconductor surface is an attractive advanced oxidation process. Several works have been done on various semiconductor photo-catalysts such as TiO_2, ZnO, Fe_2O_3, MnO_2, CeO_2, etc., for the degradation of organic and inorganic dye pollutants [1-4]. The photo-catalytic activity of a catalyst depends on crystal structure, oxidation state, surface area, band gap, etc. The activity can be enhanced by proper choice of semiconductors and also by incorporating active metal in it. SnO_2 is a wide-band-gap semiconductor and is successfully employed as a photo-catalyst for the treatment of various organic compounds as well as dye pollutants. CeO_2 and MnO_2 are low-cost and relatively harmless materials which are present in the Earth's crust. These materials present several characteristics and potential advantages for photo-catalytic applications [2].

Numerous hazardous organic compounds are discharged into the environment as a result of man-made activities. Waste water from different industries and laboratories pose great hazards to the environment. These wastes are harmful to microorganisms, aquatic lives and men. Rigorous research is being carried out to develop advanced physico-chemical methods for the detoxification of these toxic wastes from water and soil. Photo-catalysis process has received a high attention in breaking of organic compounds due to complete mineralization ability and also applicable to water pollution control employing solar light. The solar light is a renewable energy, cost effective and completely free for the photo-degradation of organic as well as inorganic dyes.

Photo-degradation of pollutants using solar light is very economically viable process since solar energy is an abundant natural energy source. The photo-catalysts chosen for the present discussion are some transition metal oxides and mixed metal oxides. The transition metal oxide materials are of interest to many due to less expensive in comparison to the precious metal

catalysts such as platinum, palladium, etc. Transition metal doping improves trapping of electrons and inhibiting electron–hole recombination during the photolysis process. The oxides catalysts are thermally stable and increase the life span of the catalyst. Insertion of transition metal ions in the photo-catalyst structure can significantly enhance the photonic efficiency by widening the light absorption range and modifying the redox potential of the photo-produced radicals. SnO_2 has been used in a wide range of applications in science, technology and industries such as catalysts, semiconductor material, gas sensing, ceramics, plastics and biomedical applications [5]. A. Pandurangan et al. [6] has studied the photo-catalytic degradation of Auramine O using ZnO as a photo-catalyst and sunlight as an illuminant. The description of the present work is about photocatalytic degradation of Auramine O and Naphthol Blue Black dyes over SnO_2 and CeO_2 doped Mn compounds using solar light.

2. Experimental

SnO_2 and CeO_2 doped Mn samples have been prepared by adopting co-precipitation method. The stoichiometric quantities of pure grade metal nitrates chemicals were taken in proportions and dissolved in distilled water. To this added 10% sodium hydroxide solution with stirring till precipitation was complete. This precipitate was digested on a water bath with the addition of 30% H_2O_2 with stirring. The precipitate was filtered and dried at 100 ºC. It was then fired at 400 ºC for 4 h. CeO_2 doped samples were then sintered in a furnace at 700 ºC for 7–10 h to form solid solutions.

Photo-catalysts prepared by co-precipitation method were characterized by XRD, FTIR and band gap measurements. Surface area of the sample was measured using BET nitrogen adsorption method. The magnetic susceptibility was determined by Gouy method at room temperature in air employing a field of 800 Gauss and using {Hg[Co(SCN)$_4$]} as a standard material. The electrical resistivity (ϱ) of the SnO_2 sample was measured by two probe method using sintered pellet from 250 ºC to room temperature during cooling cycle. The diffuse reflectance spectra of all the samples were recorded at room temperature in the 200–800 nm range using $BaSO_4$ as a reference material.

The photo-catalytic degradation of azo dyes was performed in a simple glass reactor. Aqueous solution of dye 10^{-5} M concentration was placed in the reactor; the solution was aerated with oxygen for 5 to 10 minutes then added the solid semiconductor catalyst and closed with cork or stopper to prevent loss due to evaporation. The photolysis of Auramine O dye was per-formed out using sunlight and SnO_2 as the photo-catalyst. The Naphthol blue black dye (NBB) degradation was carried out using CeO_2 doped compounds. The study was performed between 10.00 am to 4.00 pm during all sunny days. The reaction was studied for various experimental conditions such as pH, presence of oxygen, amount of catalyst, absence of catalyst, etc. The 100 ml of 10^{-5} M aqueous solution of the respective dye was aerated with O_2 and kept in sunlight with 100 mg of the photo-catalyst sample in a glass reactor. The photo-degradation rate was measured by taking the absorbance (λ_{max}) of the dye with periodic interval of time employing UV-Visible spectrophotometer.

3. Results and discussion

SnO_2 was characterized by recording the X-ray diffraction pattern and the d_{hkl} and 2θ values obtained were checked with the reported values in the literature (ICDD-PDF data files). Figure 1 shows the XRD pattern of SnO_2 sample prepared at 400 °C. SnO_2 is having tetrahedral structure. Particle size determined by Debye Scherer's equation was found to be from 20-50 nm.
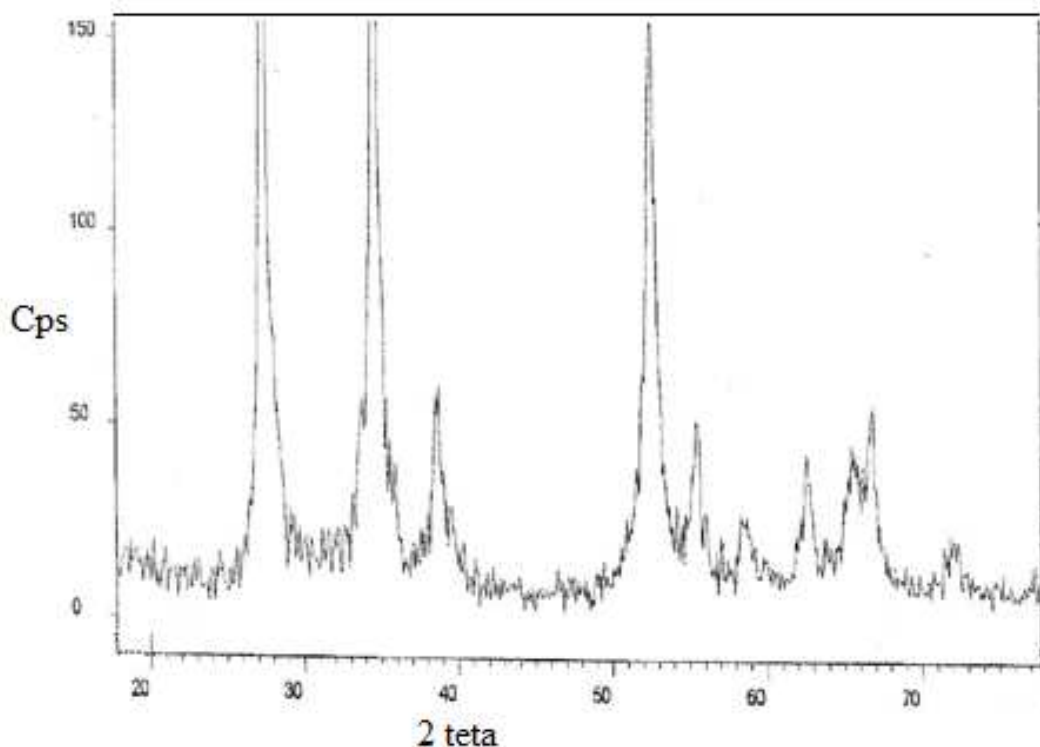

Figure 1. XRD pattern of SnO_2.

Thermal study of dried hydroxide sample shows that $Sn(OH)_4$ decompose at around 120°C which is indicated by endothermic peak in thermal analysis. The surface area measured by using BET nitrogen adsorption method is found to be 8.05 m^2/g. The FTIR study was performed aiming to ascertain the metal oxygen bond in SnO_2 sample. The two broad bands were observed at 610 and 680 cm^{-1} assigned to Sn-O stretching vibrational modes, which is in agreement with literature data [7]. Magnetic study performed at room temperature indicates that SnO_2 is diamagnetic in nature as reported earlier.

The electrical resistivity of the sample was measured by two probe method during cooling cycle from 250°C to room temperature. Variation in electrical resistivity with temperature for SnO_2 sample is shown in Figure 2. The electrical resistivity decreases with increase in temperature showing semiconductor behaviour. SnO_2 is n-type semiconductor, since oxygen vacancies or interstitial Sn^{+4} is donor site [8]. Figure 3 shows UV-Visible reflectance spectra of SnO_2 sample. The spectrum consists of single, broad intense absorption in visible region

ascribed to a charge transfer process from the valence band to the conduction band. The DRS spectrum provides the band gap of SnO_2 equal to 3.5 eV which is in good agreement to the reported value.
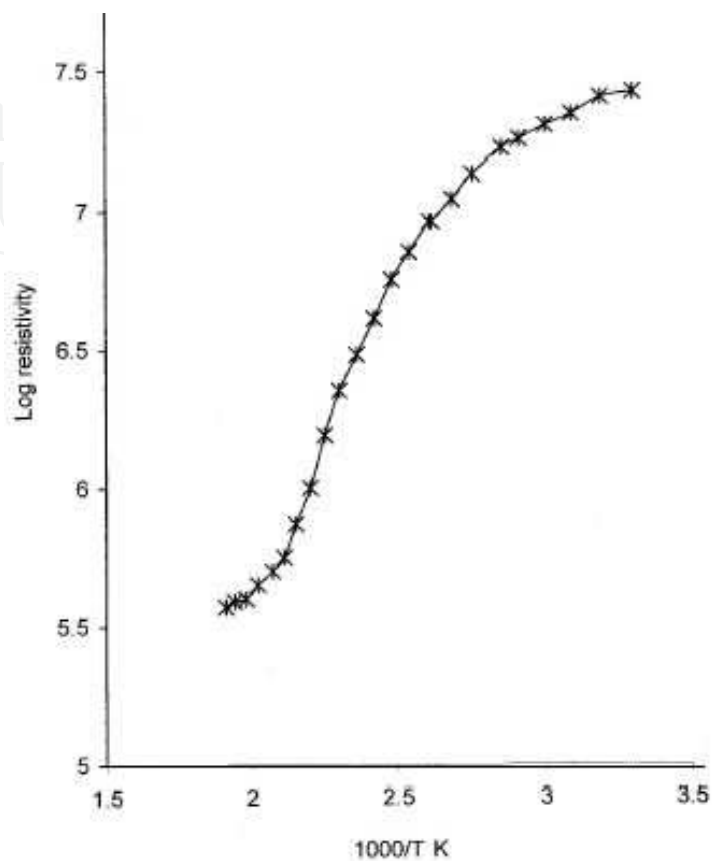

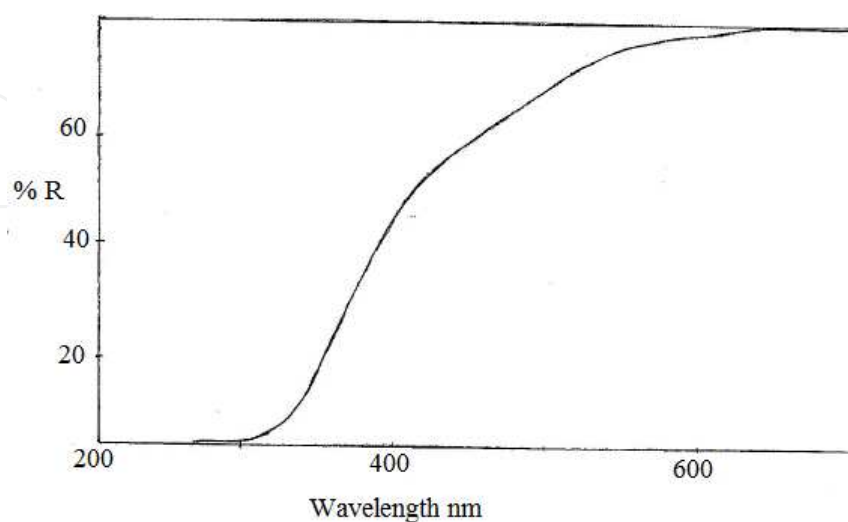**Figure 2.** Variation of electrical resistivity with temperature of SnO_2.

Figure 3. UV-Visible diffuse reflectance spectra of SnO_2.

The photo-catalytic degradation of the Auramine O dye was performed using prepared SnO_2 photo-catalyst. The complete UV-Visible spectrum of the dye is shown in Figure 4. The dye has absorption in the visible region at λ_{max} 432 nm. The progress of photo-catalytic degradation is monitored by measuring the absorbance of the solution at this wavelength.
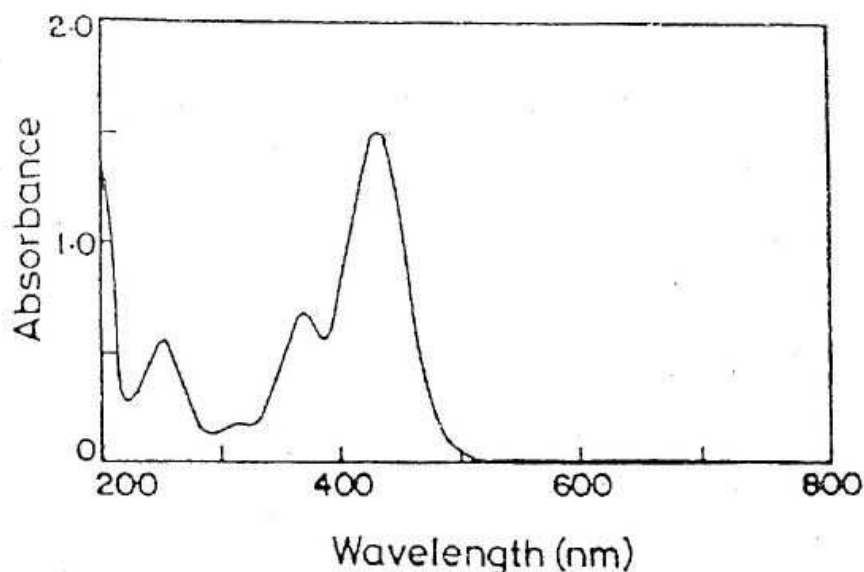

Figure 4. UV-Visible spectrum of Auramine O dye.

The optimum amount of the catalyst for photo-catalytic degradation of Auramine O dye was found to be 100 mg for 100 ml of the solution as shown in Figure 5. The reaction was studied with different experimental conditions like pH, amount of catalyst, oxygen, etc. The rate of dye degradation increases with the amount of the photo-catalyst, but after a certain limit if the amount is increased further, there will be a saturation point. The amount of photo-catalyst affects both the number of active sites on the photo-catalyst and the penetration of light through the suspension [9]. Also increased amount of photo-catalyst increases the rate of deactivation of activated molecules by collision with ground state photo-catalyst.

In the absence of oxygen, the photo-catalytic degradation of the dye was negligible. Oxygen is an electron scavenger [10] which traps the photo-generated electrons from the conduction band and thus preventi the electron–hole recombination. Dissolved oxygen traps the conduction band electrons forming superoxide ion (O^{2-}). Also the dye degradation is negligible in absence of sunlight. Figure 6 shows the photo-catalytic degradation of Auramine O dye with time under different conditions over SnO_2 photo-catalyst. Figure 7 shows the Auramine O dye degradation over photo-catalyst at neutral pH and at different interval period. The absorption spectra obtained after complete degradation suggest that degradation products are colourless. It has been observed that degradation of dye is faster in alkaline pH, i.e. at pH 10. At higher pH, the hydroxyl radical and O_2^- can be easily diffuse from the negative surface of the semiconductor into the bulk of the reaction solution. At pH 4, the degradation activity is lower than neutral pH.
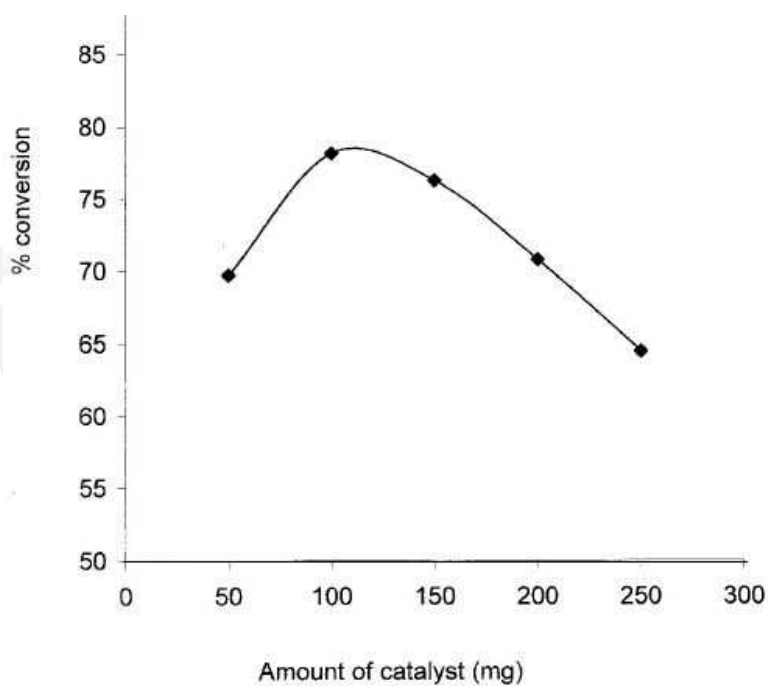
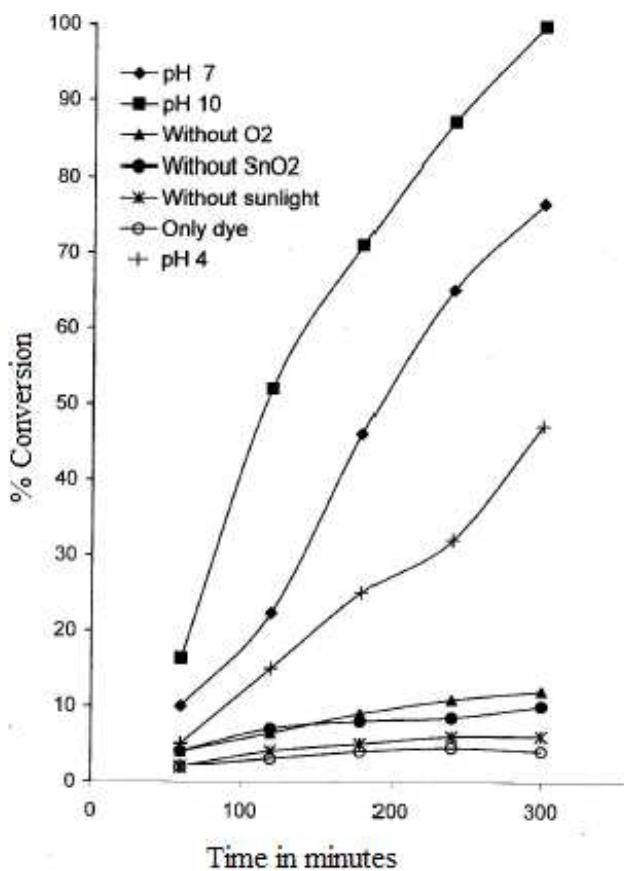**Figure 5.** Optimization of catalyst amount.

Figure 6. Percentage conversion of Auraamine O dye with time using SnO_2 photo-catalyst.
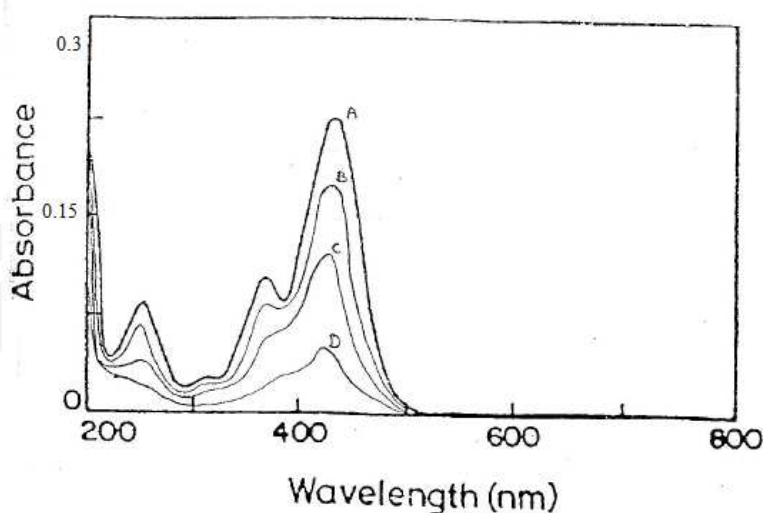
Figure 7. Auramine O dye degradation over the photo-catalyst at neutral pH with time (A) 60 min, (B) 120 min, (C) 180 min and (D) 240 min.

Photo-catalytic degradation of Naphthol Blue Black dye (NBB) was studied using CeO_2 doped Mn compounds. The Figure 8 shows the X-ray diffraction pattern of CeO_2 and some doped compounds. The NBB dye in aqueous solution has λ_{max} at 618 nm in the visible region. The absorbance of the dye solution at 618 nm monitors the progress of photo-catalytic degradation process. The photo-catalytic process was carried out at varying experimental parameters such as quantum of the catalyst, with and without aeration, with and without catalyst, with and without solar radiation and varying the pH from neutral, acidic to basic. Figure 9 depicts the representative spectra of NBB through λ_{max} in the range 400 to 700 nm with different irradiation time using CeO_2 doped Mn sample ($Ce_{0.7}Mn_{0.3}O_2$) as photo-catalyst at neutral pH. The lowering of optical density or absorbance was observed with time by sun light irradiation. This conveys that the rupturing of conjugation bonds of the dye take place due to solar radiation with the photo-catalyst, giving colourless product. It was found that 100 mg was the optimum weight of catalyst required in this photo-catalytic reaction for 100 ml of the dye solution. Normally the rate of dye degradation reaction goes up with the amount of catalyst mainly due to the increase in the exposed surface area of the catalyst. If the weight of the photo-catalyst increases beyond a certain weight (100 mg), there will be a saturation point. As per Kartal et al. [9], the quantum of photo-catalyst influences both the number of active sites and the passage of light through the suspension. Oxygen takes the electron which was migrated to conduction band due to photon irradiation, and if there is no oxygen, electron–hole recombination takes place lowering the dye degradation rate. Therefore, oxygen is very essential in photo-degradation process. Oxygen scavenges the photo-generated electrons from the conduction band generating O_2^- ions ($O_2 + e^- \rightarrow O_2^-$) [11].

Dye degradation was studied at different pH conditions, which is one of the important factors. It has been observed that photo-degradation rate is higher in alkaline pH, i.e. at pH 10. At higher alkaline pH there is more possibility for the formation of hydroxyl radical ($OH^·$), which helps photo-degradation process of the dye. Hydroxyl radical acts as an oxidant thereby
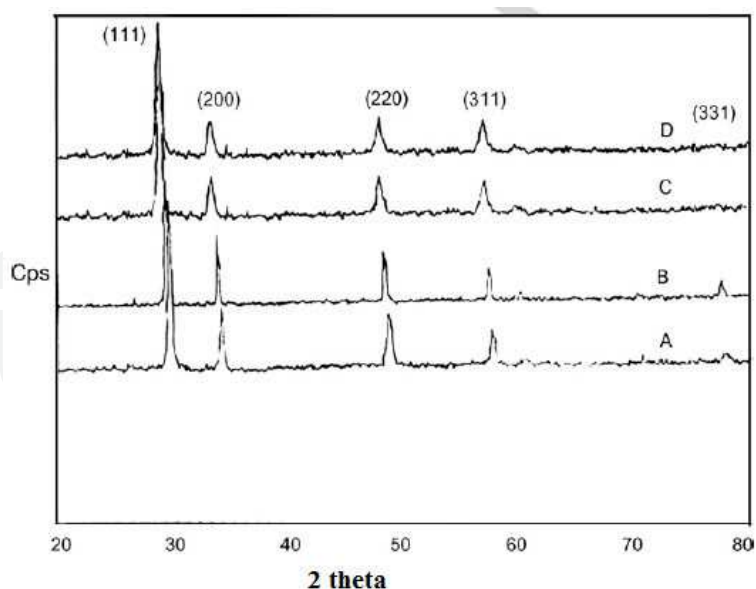
Figure 8. XRD powder pattern of CeO_2 doped Mn: (A) CeO_2, (B) $Ce_{0.9}Mn_{0.1}O_2$, (C) $Ce_{0.8}Mn_{0.2}O_2$ and (D) MnO_2.
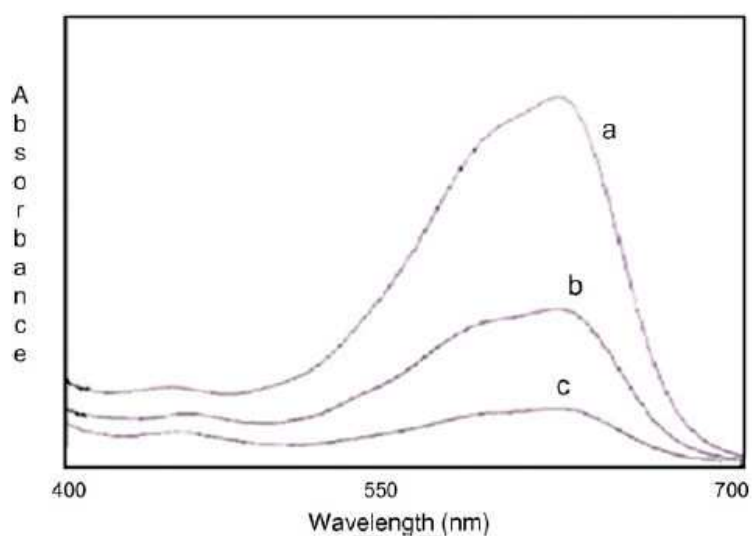

Figure 9. Absorption spectra of NBB dye degradation at λ_{max} range with time over $Ce_{0.7}Mn_{0.3}O_2$: (a) after 1 h, (b) 3 h and (c) 4 h irradiation.

increasing the rate of degradation. By increasing the pH of the dye solution from 4 to 10 enhances the photo-catalytic process. The photo-catalytic degradation reaction was higher in alkaline pH than in acidic pH. In alkaline pH the number of hydroxyl ions are more, the negative surface of the photo-catalyst with OH^- ions behaves as an efficient trap for the photo-generated holes to produce hydroxyl radicals. Besides, the hydroxyl radical and O_2^- ions can easily diffuse from the negative surface of the photo-catalyst into the bulk solution easily at higher pH. Therefore, hydroxyl radical is main species for dye degradation. CeO_2 showed low activity for the degradation of NBB dye. But after doping with Mn, it showed increased photo-catalytic activity as seen in Figure 10 at pH 7. As the dopant (x) increases, the photo-catalytic

activity increases. Table 1 shows the calculated band gap energies of the samples. The solid solution samples showed lower band gap energies than CeO_2 and these samples of lower band gap have helped to propagate the electron from valence band to conduction band initiating photolysis reaction. Also increased magnetic susceptibility of these solid solutions is an indication of more free electrons availability than CeO_2. These are some of the factors responsible for the photo-activity besides others. Figure 11 shows the photo-catalytic degradation of NBB dye over $Ce_{1-x}Mn_xO_2$ with time at pH 10. Here also solid solutions showed higher photo-catalytic activity than CeO_2 and MnO_2, respectively.
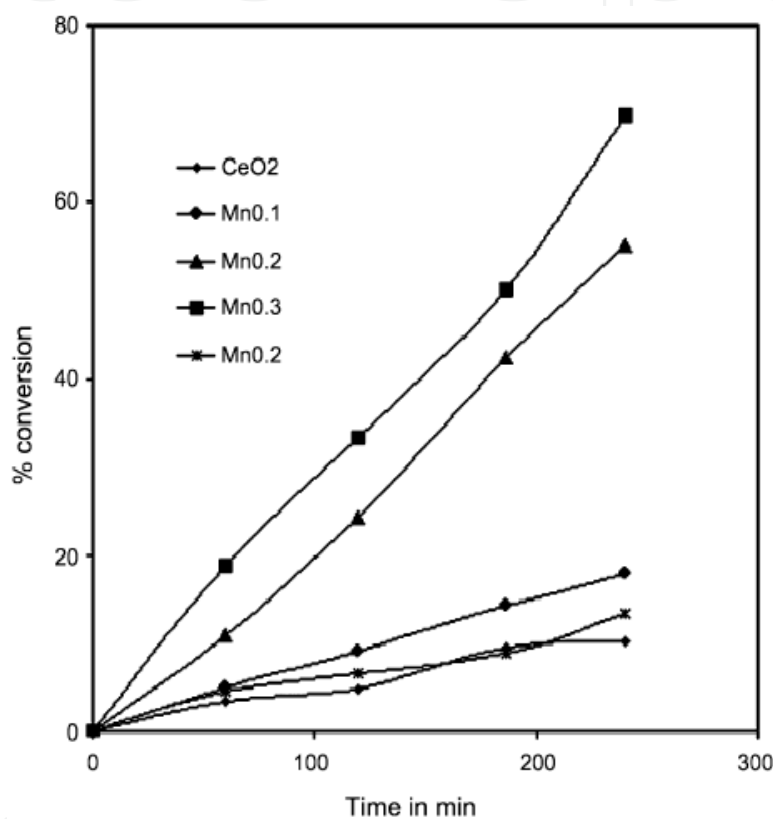

Figure 10. Photo-catalytic degradation of NBB dye with time using CeO_2 doped Mn at pH 7.

Sample	Magnetic susceptibility (χ_g cgs units)	μ_{eff} (BM)	Surface area BET($m^2\,g^{-1}$)	Band gap energy (eV)
CeO_2	2.94×10^{-6}	1.06	7.36	3.64
$Ce_{0.9}Mn_{0.1}O_2$	4.06×10^{-6}	1.21	2.75	3.20
$Ce_{0.8}Mn_{0.2}O_2$	4.98×10^{-6}	1.30	6.52	3.26
$Ce_{0.7}Mn_{0.3}O_2$	6.84×10^{-6}	1.48	8.34	3.50
MnO_2	84.98×10^{-6}	3.84	16.07	3.66

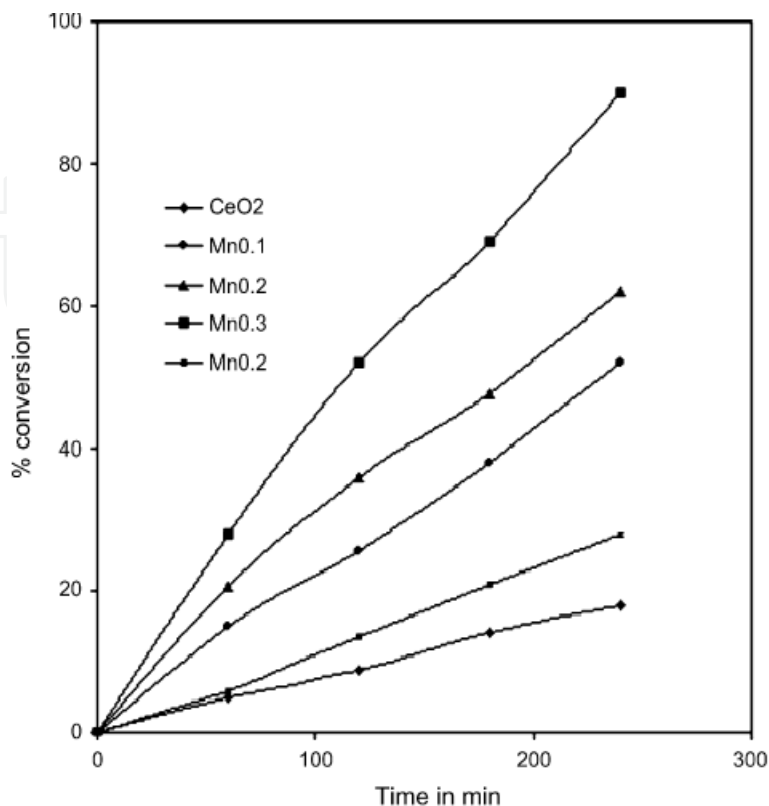**Table 1.** Magnetic susceptibility, surface area and band gap energy of $Ce_{1-x}Mn_xO_2$ samples.
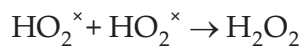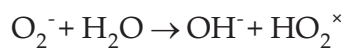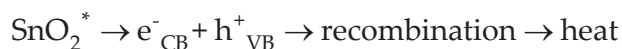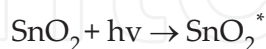
Figure 11. Photo-catalytic degradation of NBB dye with time using CeO_2 doped Mn at pH 10.

The electrons are excited when photo-catalyst is illuminated by sunlight and electrons are promoted to conduction band leaving holes in the valence band. These electrons are trapped by O_2 forming O_2^- ions. The valence band holes generate hydroxyl radicals ($OH^·$) from OH^- ions and these $HO^·$ radicals attack the dye leading to complete mineralization. Scheme I suggests one of the photo-catalytic degradation path way, which is in some agreement with the literature [10] by taking photo-catalyst SnO_2 as an example.

$$SnO_2 + h\nu \rightarrow SnO_2^*$$
$$SnO_2^* \rightarrow e^-_{CB} + h^+_{VB} \rightarrow recombination \rightarrow heat$$
$$O_2 + e^-_{CB} \rightarrow O_2^-$$
$$O_2^- + H_2O \rightarrow OH^- + HO_2^×$$
$$HO_2^× + HO_2^× \rightarrow H_2O_2$$
$$h^+_{VB} + OH^- \rightarrow OH^×$$
$$OH^× + Dye \rightarrow Degraded\ products$$
$$\left(e^-_{CB}\ is\ the\ electron\ in\ conduction\ band\ and\ h^+_{VB}\ is\ hole\ in\ valence\ band \right)$$

Heterogeneous photo-catalysis through illumination by solar light on semiconductor surface is an attractive advance oxidation process. Photo-degradation of pollutants using semiconductor photo-catalyst with solar light can make it an economically viable process since solar energy is an abundant and inexpensive natural energy source. Solar energy has been successfully used for photo-catalytic degradation of pollutants. The main advantage of the photo-catalytic process is its mild operation conditions.

It is often suggested that surface hydroxyl group play an important role in determining the photo-catalytic activity, since these species act as a traps for photo-generated holes to form hydroxyl radicals and reduce electron–hole recombination. In the photo-degradation of reactive dyes, the azo group was attached by hydroxyl group at two positions, one at the single bond C-N of the azo group and other at the double bond of the azo group. The photo-catalytic activity is influenced by several factors such as the crystal structure of the semiconductor, surface area, size distribution, band gap and surface hydroxyl group density.

4. Conclusions

Nano size SnO_2 and CeO_2 doped compounds were prepared by co-precipitation precursor method. SnO_2 is diamagnetic in nature and shows semiconductor behaviour. SnO_2 has band gap of 3.5 eV, which help in preventing the electron–hole recombination. It is found that azo dye Auramine O can be degraded efficiently using SnO_2 semiconductor photo-catalyst with solar light. CeO_2 has low photo-catalytic activity for the degradation of Naphthol Blur Black. Increase in photo-catalytic activity was noticed by incorporation of Mn in CeO_2 lattice. This is mainly due to the increase of the redox couple Ce^{4+} - Ce^{3+} and improvement of the band gap energy. The mechanism involves the formation of $OH^{.}$ radicals which are active oxidizing agents for the degradation of dyes. Also oxygen prevents the recombination of electron–hole pairs hence increasing the reaction rate. The dye degrades to a colourless solution after irradiation.

Acknowledgements

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